

MEMS-based Force-detected Nuclear Magnetic Resonance Spectrometer for *In situ* Planetary Exploration

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Abstract—Nuclear Magnetic Resonance (NMR) is a well-known spectroscopic technique used by chemists and is especially powerful in detecting the presence of water and distinguishing between arbitrary physisorbed and chemisorbed states. This ability of NMR is of particular importance in the search for extra-terrestrial life on planets such as Mars, where there are strong indications that liquid water exists or has existed previously. However, the conventional room-sized NMR instrument is precluded from ever being considered as a planetary instrument.

Proof-of-principle for a novel, MEMS-based (MEMS is the acronym for Micro Electro Mechanical Systems) NMR spectrometer was recently demonstrated. In contrast to conventional NMR spectroscopy, which involves the detection of radiofrequency (rf) magnetic flux, the force-detection technique works on the principle of using rf excitation to resonantly invert the magnetization of the sample of interest. Applications of FDNMR spectroscopy in planetary exploration will be discussed.

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1. INTRODUCTION

Nuclear Magnetic Resonance (NMR) is the premier spectroscopic technique for the study of molecular structure and dynamics in condensed matter. This paper describes the development of a miniature NMR instrument for NASA's *in situ* planetary exploration missions. The mineralogical [1] and astrobiological applications of NMR are of interest to NASA. NMR is uniquely capable of distinguishing between arbitrary physisorbed or chemisorbed states of water. This capability is particularly useful in the search for the signatures of extant/extinct life on other planets since life as we know it on earth is intimately linked to the presence of water. The composition of minerals containing elements with non-zero nuclear spin [1], including protons, can also be obtained using NMR. Figure 1 shows a schematic representation of the basic working principle of NMR spectroscopy for a sample containing nuclei with spin $1/2$. The sample is placed within a uniform, external magnetic field B_0 , which causes Zeeman splitting of the degenerate spin energy levels. The excitation energy ($h\nu$) required for inverting the nuclear spins is supplied by the radiofrequency (rf) excitation coil. The power of NMR spectroscopy comes from the fact that the Zeeman interaction is a sensitive probe of the chemical bonding environment of the nuclei since the local electronic structure can perturb the magnetic field around the nuclei. The traditional Faraday-law detection technique depends on the excited spins inducing a current in a nearby rf coil as they precess about the external magnetic field vector. The sensitivity or signal-to-noise ratio (SNR) of the traditional inductive detection technique is given by the ratio of the induced current

(signal) to the Johnson noise in the coil. The SNR for the inductive detection technique scales as the square of the sample radius.

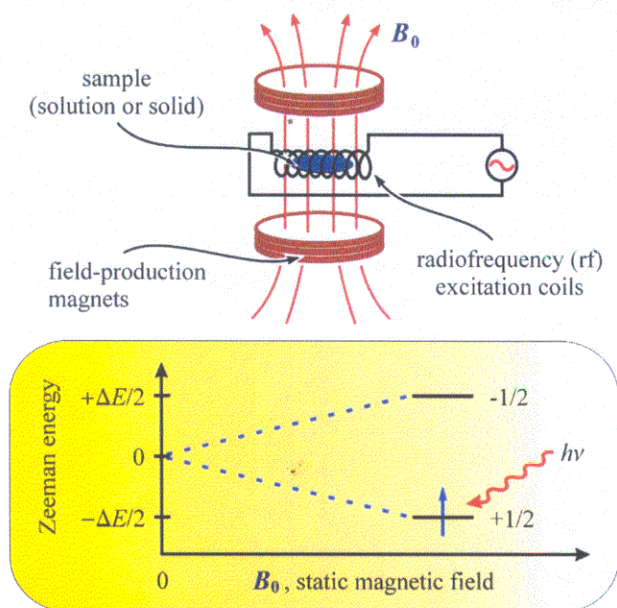


Fig. 1. Schematic diagram showing the Nuclear Magnetic Resonance (NMR) spectroscopic measurement of a sample containing atoms with nuclear spin = $1/2$. The uniform magnetic field B_0 causes Zeeman splitting of the degenerate spin energy levels in the sample. The sample is placed within a radiofrequency (RF) excitation coil that supplies the RF energy ($h\nu$) required for exciting the nuclear spins. The local electronic structure can perturb the magnetic field around the nuclei, thus making the Zeeman interaction a sensitive probe of the chemical bonding environment of the nuclei.

An alternative detection technique (Figure 2) is force detection, in which a dipole-dipole force is measured between a fixed sample containing nuclear spins and a harmonically bound ferromagnetic oscillator. As shown in Fig. 2, the ferromagnetic oscillator is made up of a detector magnet mounted on a micromachined Si beam. The key innovation is to make the detector magnet part of a disk-shaped magnet structure that provides a nominally homogeneous field over the entire sample volume. In contrast to other force-detection methods, such a device exhibits better observation of magnetization, enhanced resolution, and no gradient (BOOMERANG) [2]. The detector magnet's shape and size are each optimized for sensitivity to the force of the sample's gradient magnetic field acting on the detector's magnetic moment. The dipole force is modulated at the mechanical resonance frequency of the ferromagnetic oscillator rf pulses during the NMR experiment. The SNR for measurements of the mean spin magnetization of samples falls as the square root of the sample radius and hence more slowly than the inductive detection technique (see Figure 3) [2]. The cross-over in sensitivity for typical samples occurs at sample sizes of just below 1 mm. Thus the force detection technique, which is amenable to MEMS-type miniaturization, is more sensitive than a room-sized conventional NMR instrument at sample

sizes less than 1 mm. Also, since the entire sample is subject to the same static magnetic field, multiple-pulse NMR experiments with spectroscopic resolution are possible. The force detection technique is compatible with modern rf excitation sequences that can provide a detailed picture of the chemical bonding in a given sample. Finally, if desired, a gradient can be reintroduced during evolution periods for imaging purposes.

2. OBJECTIVES AND SIGNIFICANT ASPECTS

NASA is interested in the development of a low-mass, low-power, portable NMR instrument for *in situ* planetary exploration with astrobiological or mineralogical emphasis. The primary objective of the JPL development project funded by NASA's Cross Enterprise Technology Development Program/Breakthrough Sensors and Instrument Components Thrust is to develop a MEMS-scale force detected NMR (FDNMR) spectrometer. The high-resolution FDNMR spectrometer is designed for measuring samples with sizes in the 10 to 100- μm range. The sensor has a magnet mass of less than 1.5g, a volume of less than 0.5 cm^3 and consumes less than 100 mW of power. The chemical information that can be potentially obtained by this FDNMR spectrometer is listed below:

- Identification of ^1H species (H_2O , OH^-) and bonding environment
- Chemically specific identification of biological molecules
- Bond lengths, bond angles, cation disorder (e.g., aluminosilicates)
- Mineral identification through local bonding effect, even in amorphous phases

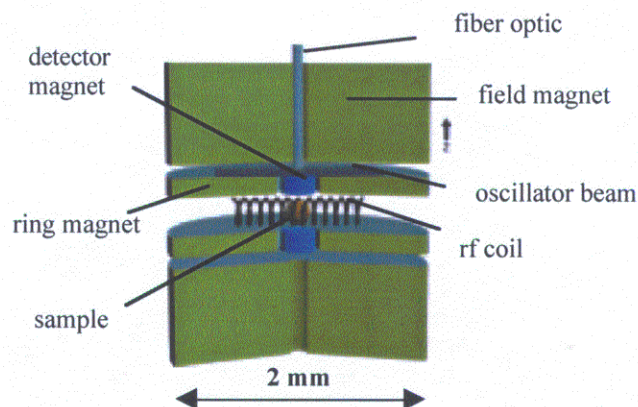


Fig. 2. Schematic diagram of the proposed MEMS-based Force Detected Nuclear Magnetic Resonance (FDNMR) Spectrometer. The spectrometer is a 2 mm diameter device capable of measuring 60-micron-sized particles. The sample sits in a static, homogeneous field provided by the novel BOOMERANG magnet assembly. Rf irradiation of the sample allows for arbitrary NMR pulse sequences including a period during which the longitudinal nuclear magnetization is cyclically inverted at the mechanical resonance frequency of the oscillator. The sub-angstrom motion of the detector magnet due to the dipole-dipole interaction with the sample is detected by interferometry via the fiber optic.

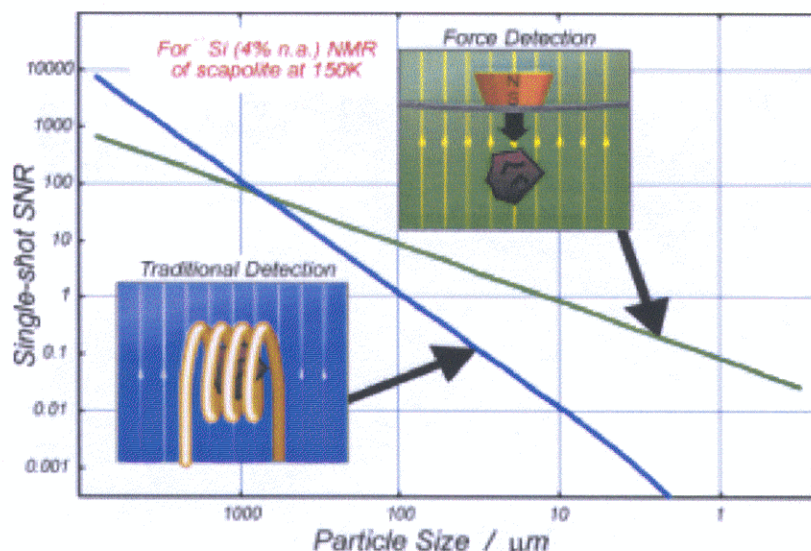


Fig. 3. A comparison of the sensitivity (as represented by single-shot signal to noise Ratio (SNR)) of the traditional, inductive detection technique versus the force detection technique. The SNR is plotted versus the size of a scapolite sample containing ^{29}Si atoms (4% native abundance) with spin 1/2. The measurement is simulated for a Martian ambient temperature of 150K. For a particle with diameter d the SNR for traditional inductive detection scales as d^2 whereas the SNR for force detection scales as $d^{0.5}$. Thus at particle sizes below 1 mm, the sensitivity of the force detection technique is superior to that of the inductive detection technique.

3. TECHNICAL APPROACH

The development of the MEMS-based FDNMR spectrometer is being pursued on two fronts. The first approach is the relatively rapid assembly and testing of a prototype spectrometer using mostly conventionally machined parts. The proof-of-principle demonstration was conducted using the BOOMERANG prototype spectrometer. The prototype is 25 times the linear size of the final MEMS spectrometer and is used to make measurements on a 3-mm sized sample. From a sensitivity standpoint (see Figure 3) the prototype is not at the optimum size scale for FDNMR measurements. However, the prototype spectrometer can still be used to refine the experimental protocols and to optimize the spectrometer parameters. The second approach, namely the design and fabrication of the MEMS spectrometer, is also being carried out concurrently with the prototype spectrometer development.

A schematic block diagram showing the major components of the prototype spectrometer is shown in Figure 4. A predetermined RF pulse sequence is supplied to the sample via the RF coil. The motion of the ferromagnetic harmonic oscillator in response to the inversion of the sample magnetization is measured using fiber optic interferometry and subsequently digitized.

Prior to performing NMR experiments, it is extremely important to minimize the various sources of noise and error that can degrade the SNR since NMR signals are inherently very weak. The spectrum is averaged over multiple scans and it is essential that the spectrometer be stable over long measurement times. Sources of noise and error include electronics noise, poor RF quality, laser noise, and low

quality factor and thermal drift of the oscillator frequency. Extensive work goes into identifying and minimizing the sources of noise and error.

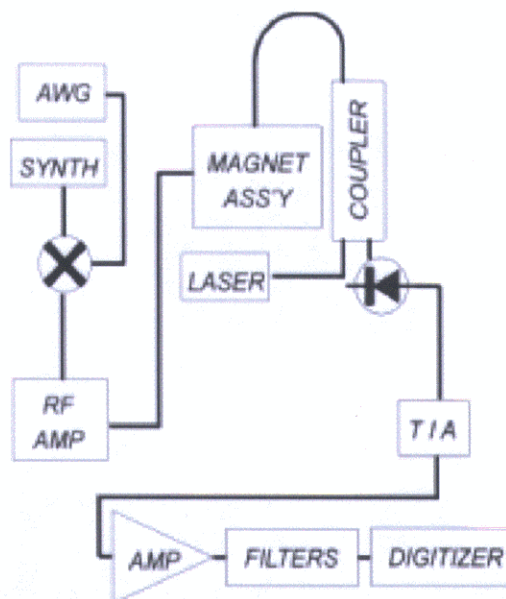


Fig. 4. Block diagram showing the major components of a FDNMR spectrometer. The NMR magnets and mechanical oscillator detector are contained in the "Magnet Assembly" box. The RF excitation is provided by the RF amplifier (RF Amp) which amplifies the RF pulses (Arbitrary Waveform Generator + Synthesizer). The movement of the harmonic oscillator is measured using fiber optic interferometry, amplified by the transimpedance amplifier (TIA), and subsequently digitized.

NMR Spectrum measurement

The NMR spectrum is acquired using a sequence of steps. The first step is the encoding of the NMR, which consists of the sample being irradiated by two $\pi/2$ RF pulses separated by a delay time. The action of the first $\pi/2$ pulse is to rotate the sample magnetization from the longitudinal direction to the horizontal plane. Following a time "t", allowing the nuclear spins to "evolve" as they precess about the longitudinal axis, a second $\pi/2$ pulse is applied causing the surviving component of the magnetization to be rotated in the longitudinal direction. The magnetization is then cyclically inverted at the mechanical resonance frequency of the ferromagnetic harmonic oscillator. Subsequently, a fourier transform is applied to the digitized, optically detected oscillation of the sensor magnet. The fourier transform produces a peak at the mechanical resonance frequency of the harmonic oscillator. The peak contains amplitude and phase information that are plotted vs. the time interval between the encoding pulses on a "Free Induction Decay" (FID) curve. A second fourier transform of the FID curve produces the NMR spectrum of the sample [2].

MEMS FDNMR Spectrometer Development

The design and fabrication of the MEMS FDNMR spectrometer was undertaken. As mentioned previously, the design was optimized for the measurement of 60-micron-sized samples. The MEMS spectrometer consists of a 6 μm thick, 40 μm diameter sensor magnet, surrounded by a 2 mm diameter annular magnet. Figure 5 contains a summary of the fabrication process listing some of the key steps. The detector and annular magnets are electroplated within molds of photoresist on a Si wafer substrate. Just as in the prototype spectrometer, the annular magnet (Fig. 6) is fabricated with slits in it, in order to reduce eddy current damping effects. The Si beam (400 μm x 60 μm x 5 μm) for the harmonic oscillator is constructed by lithographic patterning and etching the backside of the wafer using a combination of wet chemical etching with KOH solution and a deep reactive ion etching (DRIE) process (Fig. 7). To prevent the buckling of the Si beam due to magnet stress, a 20- μm -thick Si "buttress" is created on the beam under the detector magnet.

4. RESULTS AND CONCLUSIONS

Prototype FDNMR Spectrometer Experiments

In order to better predict design issues for a MEMS FDNMR spectrometer and to prove the concept of force detection of NMR, a macro-scale prototype was built. This device has yielded NMR spectra on several solid and liquid samples, including liquid water [3]. Possible problems for a MEMS device have been observed at the millimeter size scale and improvements to the MEMS designs are ongoing.

A notable observation was that of substantial eddy-current damping of the mechanical oscillator, causing lower sensitivity NMR detection than predicted. Experiments using slitted magnets to break up the conductors responsible for eddy currents have led to modification of the MEMS process to reduce the eddy currents on the micron scale.

Additionally, moving detection electronics and laser supply to 24V battery power produced substantial improvement in system noise floor and allows for a more accurate simulation of *in situ* spectrometer operation.

MEMS FDNMR Spectrometer Design and Fabrication

A 26-step process was developed for the fabrication of the integrated ferromagnetic harmonic oscillator and magnet assembly. A one-step plating process [4] was arrived at iteratively to produce the 6- μm -thick detector and ring magnet assembly. A photolithography process was developed to achieve the 10:1 aspect ratio for the sacrificial photoresist features that formed the gap between the detector and ring magnets as well as the slits in the sensor magnet (Figure 6). A 3-component (Fe-Ni-Co) electroplating process has been developed to produce electroplated magnet structures that have a high saturation magnetization and yet are not susceptible to corrosion via rusting. A tertiary alloy film composed of approximately 50% Fe, 10% Ni and 40% Co was successfully electroplated. The saturation magnetization was measured to be approximately 2 Tesla/ μ_0 . The advantage to having higher static magnetic fields is that the NMR peaks are better separated and hence more easily resolvable.

A combination of wet KOH etching and DRIE processing was developed to thin the backside of the Si substrate wafers and to produce the Si beam with the buttress structure for the harmonic oscillator (Figure 7). A first Si wafer run of the entire 26-step process was performed and minor problems in the fabrication were discovered. These included the misalignment of the sensor magnet with respect to the Si beam and "closure" of the gap between the sensor and ring magnets during electroplating as a result of photoresist erosion. However, these problems are not considered to be insurmountable and a second fabrication run has been initiated incorporating improvements to solve the above-mentioned problems.

In conclusion, it has been shown that through the use of a novel device configuration, a powerful spectroscopic tool for chemical and biological analysis can be added to NASA's arsenal of micro-instruments. The proof-of-principle for the FDNMR has been demonstrated using the prototype instrument. Additional NMR experiments have also been performed using the prototype. The ultimate MEMS-version is currently under fabrication.

5. REFERENCES

- [1] R.J. Kirkpatrick, Reviews in Mineralogy 18, 341 (1998)
- [2] G.M. Leskowitz, L.A. Madsen, and D.P. Weitekamp, Sol.St. Nucl.Magn.Reson. 11, 73 (1998)
- [3] L.A. Madsen, G.M. Leskowitz, and D.P. Weitekamp, "Observation of Force Detected NMR in a homogenous field", manuscript in preparation, October, 2000.
- [4] E.E. Castellani, J.V. Powers, L.T. Romankiw, IBM, US Patent 4,102,756,1978.

1. Thermal oxidation and patterning for sacrificial layer.
2. Deposit Cr/Au (200Å/1000Å) plating seed layer and pattern photoresist mold.
3. Electroplate ring and detector magnets 10 μm thick.
4. Protect front side by wax-mounting to wafer.
5. Pattern back and create stress buttress and oscillator beam using deep RIE.
6. Remove sacrificial oxide (BOE).
7. Bond field magnet and fiber to back.

 silicon	 protect wafer
 plated magnet	 field magnet
 oxide	 photoresist
 seed layer	 fiber

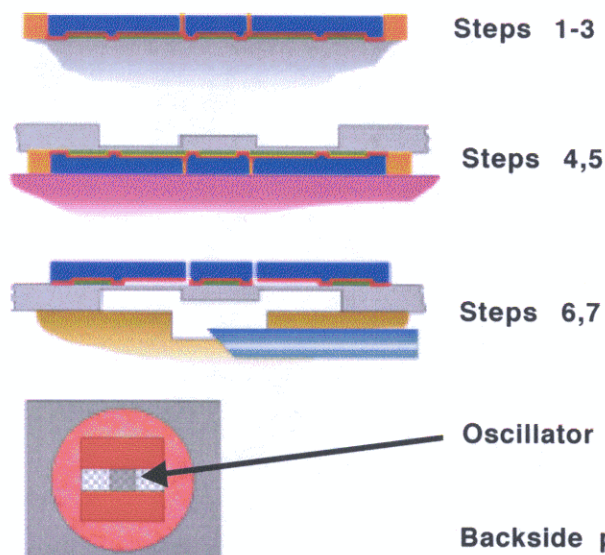


Figure 5. Process flow for the microfabrication of the MEMS FDNMR spectrometer. The process involves the electroplating of the detector and annular magnet structures and the fabrication of the si beam oscillator using deep reactive ion etching (DRIE).

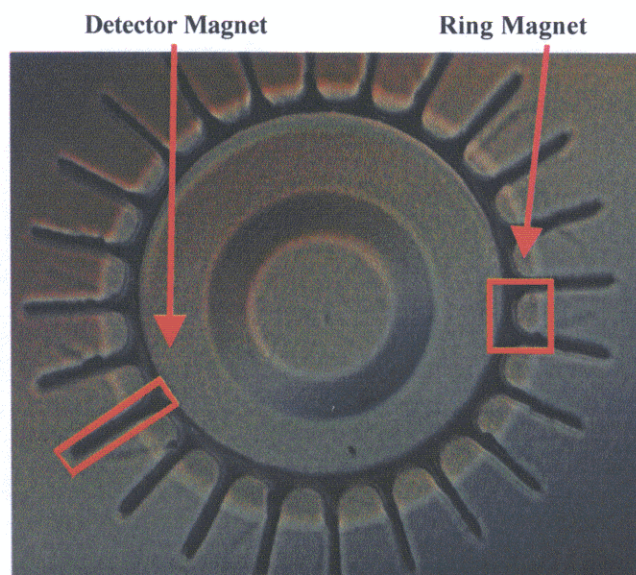


Figure 6. Close-up view of the electroplated detector and ring magnet structure for the MEMS FDNMR spectrometer. The ring magnet has slots to reduce eddy current losses (shown in the rectangular box). The gap between the ring and the detector magnet (shown in the square box) is approximately 1 μm .

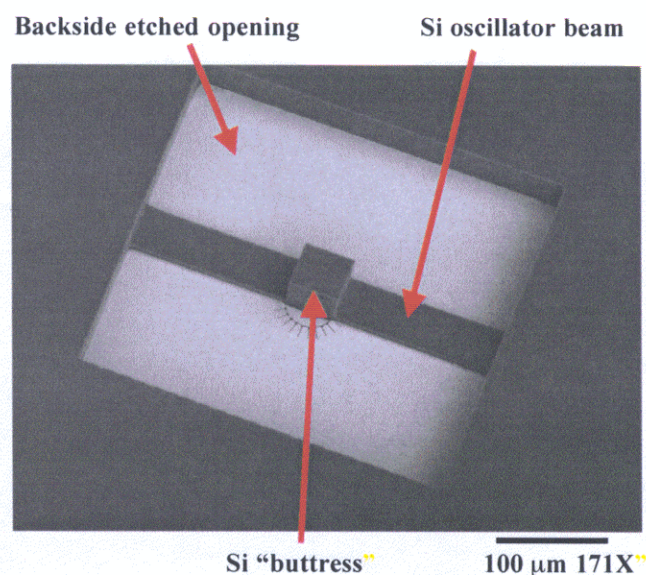


Figure 7. Microfabricated Si beam for the ferromagnetic harmonic oscillator. The beam dimensions are 400 μm x 60 μm x 5 μm . A 25- μm -thick Si "buttress" is fabricated on the beam to prevent twisting due to torsional stresses from the plated detector magnet on the front side.

6. ACKNOWLEDGEMENTS

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7. BIOGRAPHIES

Thomas George is the Supervisor of the MEMS Technology Group at the Device Research and Application Section at JPL. He received his Ph.D. in Materials Science from the University of California at Berkeley (UCB). Prior to joining JPL he worked on the transmission electron microscopy of semiconductor materials as a postdoctoral researcher at UCB and Intel Corporation, as well as the Nagoya Institute of Technology, Japan. He joined JPL in 1990, where he set up and operated an HRTEM laboratory and managed tasks aimed at the development of AlGaIn-based, solar-blind, ultraviolet detectors. He has successfully commercialized a JPL-developed, bulk Si-micromachined tunneling infrared detector. He currently manages the MEMS Technology Group with diverse MEMS-based projects and is also the task manager of programs aimed at the development of an Atmospheric Electron X-ray Spectrometer and a Force Detected NMR microinstrument for planetary exploration. He has authored/co-authored over 40 archival journal publications and holds 4 U.S. patents.

Louis Madsen is a graduate research assistant, working toward his Ph.D. in the Department of Chemistry at the California Institute of Technology. He is responsible for the design, fabrication and testing of both the prototype FDNMR as well the MEMS-based FDNMR spectrometer. He carried out the first successful proof-of-principle experiments as well as the spin-echo experiments using the prototype FDNMR instrument. He modified the MEMS fabrication process and simplified it from the original 42-step process to the current 26-step process. He is currently involved in the microfabrication of the simplified integrated ferromagnetic oscillator design.

Weilong Tang received his Ph.D. in Polymer Chemistry from the Pennsylvania State University. He is currently a consultant for the MEMS FDNMR development project at JPL. His expertise both in the microfabrication of Silicon structures as well as in the electroplating of magnetic thick films has been invaluable for the project.

Garett Leskowitz is a graduate research assistant, finishing his Ph.D. in the Department of Chemistry at the California Institute of Technology. He is responsible for the ground-breaking ideas and theoretical work behind the FDNMR (BOOMERANG) concept and spectrometers. He designed and assembled many components of the proof-of-principle prototype, and contributed greatly to the experimental data collection. Gary has also been a major force in refining the MEMS fabrication process.

Daniel Weitekamp is an Associate Professor in the Department of Chemistry at the California Institute of Technology. He received his Ph.D. in Chemistry from the University of California at Berkeley in 1982 in the area of multi-dimensional and multiple-pulse NMR, especially of solids. After postdoctoral work in ultrafast optical spectroscopy at the University of Groningen in the Netherlands, he joined the Lawrence Berkeley Laboratory as a Divisional Fellow. Since 1985 he has directed a program of graduate research in the Department of Chemistry at Caltech with an emphasis on novel methods to extend the reach of spectroscopy to otherwise inaccessible materials. He holds four US patents on spectroscopic methods, has published widely in such areas as nonlinear optical spectroscopy, zero-field and multiple-quantum NMR, optical and force detection of magnetic resonance, and the effects of quantum motion on lineshapes. His work has been recognized by the Dreyfus Teacher-Scholar Award, the R&D 100 Award, the Sloan Foundation Fellowship, and the Special Creativity Extension of the National Science Foundation.